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FOUNDATION

DEPARTMENT OF GLASS AND CERAMICS

EMR SLAG - PHASE I
(66001)

PHASE I -- FINAL REPORT

A STUDY OF THE HIGH TEMPERATURE ELECTRICAL CONDUCTIVITIES OF SILICATE SAMPLES - MOLTEN STATE

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TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	METHOD	1
3.	EXPERIMENTAL DATA	4
	APPENDIX A - AC THEORY	17

1. INTRODUCTION

The objective of this program is to measure the electrical conductivity of silicates, over the temperature range from 300°C to 1500°C. This temperature range includes regions where the silicates are solid and regions where they are molten. As such, the program was divided into two phases: the first phase involves the measurement of the electrical conductivity in the molten state up to 1500°C; and, the second phase involves the measurement of the electrical conductivity from 300°C to the softening point of the solid phase. This report covers the work carried out in Phase I of the program.

2. METHOD

The electrical conduction mechanism in most glasses is usually ionic. This is particularly true when the glass contains mobile ionic species such as the alkali ions. There may be some electronic contribution to the total electrical conductivity when multivalent transition metal ions are present in the glass. Electronic conduction then occurs in the form of a valence exchange between ions of different valence.

The electrical conductivity (or resistivity) is usually determined from the measurement of the electrical resistance. The conductivity is related to the resistance by a geometric factor depending on the measurement configuration,

$$\frac{1}{\sigma} = \rho = \text{G.F.} \times \text{Resistance}$$

For flat parallel arrangement of electrodes, the geometric factor is

$$\text{G.F.} = \frac{\text{Area}}{\text{Distance}}$$

The electrical resistance determined from measurements of the current and voltage through the system. The current and voltage are related through Ohm's law

$$V = IR$$

This relies on the linearity of the relation between the voltage and the current and the use of essentially infinite sources and sinks of charge carriers for electrodes. Most electrodes do not satisfy this condition and results in the polarization or "charging-up" at the electrode-sample interface. As a result, most of the voltage drop is across this polarization region and the simple application of Ohm's law is not valid.

Measurements using direct current cannot avoid this problem since the polarization region will grow with time leading to time dependent current or voltages. Measurements made using alternating current prevent the growth of the polarization region. However, a two-terminal measurement still includes the impedance* due to the polarization region.

In order to avoid the polarization region, the impedance can be measured using a four-terminal geometry. That is, the voltage is measured on electrodes other than the current electrodes. In the four-point in line measurement shown in Figure I, the two outer electrodes carries the

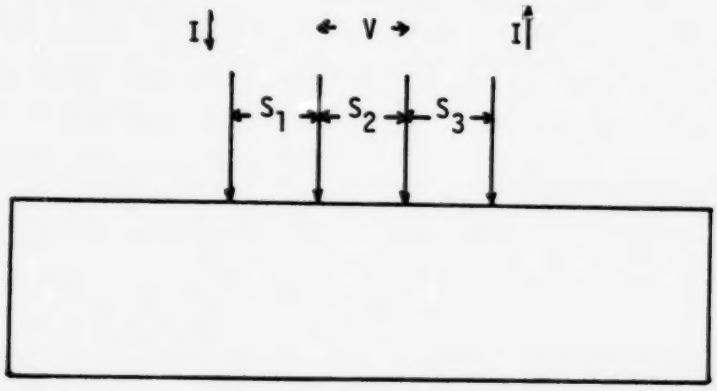


FIGURE I: FOUR TERMINAL MEASUREMENT

current, while the voltage is measured on the two inner electrodes. The resistivity** is then given by -

---

* A short discussion of ac theory is given in Appendix I.

** See, for instance, L. B. Valdes, Proceedings of the IRE, (February, 1954) p. 420

$$\rho = \frac{2\pi \ V/I}{\frac{1}{S_1} + \frac{1}{S_3} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}}$$

Normally, the distances between electrodes are made equal, $S_1 = S_2 = S_3 = S$; and

$$\rho = 2\pi \ S \ V/I$$

For measurements of the resistivity in the molten state, a resistivity probe made of four Pt-10% Rh wires was constructed and arranged in line with a nominal separation of 5mm. This is the major source of error in the measurement since the precision in which the distance can be set produces an uncertainty estimated at 20%. Thus, absolute values of the resistivity can only be quoted at 20% whereas relative measurements within the same series and on the same sample will have uncertainties of less than 10%.

A block diagram of the measurement system is shown in Figure 2. The frequency is set at 4.2 Hz, the lowest available to prevent material dispersion from contributing to the measured values. This was determined initially and no dispersion can be detected up to 21 Hz in all cases and up to 2.1k Hz for the lowest resistivity material.

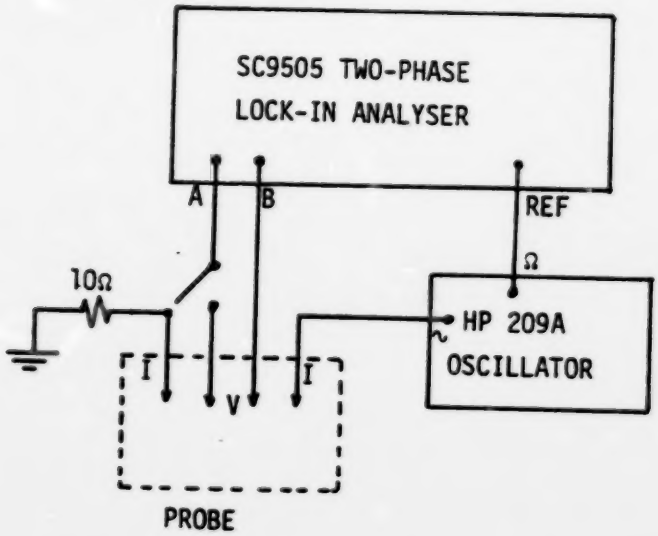


FIGURE 2: BLOCK DIAGRAM OF MEASUREMENT SYSTEM

The current is measured by the analyzer when input A is in the position shown in the figure. Measurement of the voltage is made by moving input A to the voltage position and setting the analyzer to measure A-B.

The usual procedure followed in the measurements was the following:

a) Set temperature to highest desired (limit of 1550^{o}C) and allow molten sample to come to equilibrium.

b) Lower the probe until the wires just break the surface of the molten sample.

c) A series of measurements are made at varying currents and voltage making sure that the current-voltage relationship remains linear.

At large currents, the polarization region can extend to the voltage probes giving non-linear behaviour and large effective resistance.

d) A least-squares analysis of the data yields a slope which is the measured value of the resistance at the temperature. This multiplied by the geometric factor yields the resistivity.

e) The temperature is reset to a lower value and the measurement cycles to C.

The temperature was measured by a Pt-Pt 10% Rh thermocouple which also breaks the surface of the melt. The uncertainty in the temperature measurement is ± 3^{o}C.

If at any time, the sample solidified, it is indicated by a large increase in resistance. To remelt the sample and recover the measurements, it is necessary to re-set to the highest temperature and lower the temperature after equilibrium has been reached.

3. EXPERIMENTAL DATA

A total of 24 samples were received from the scientific authority. These are the following:

1. 202.5g trap rock + 97.5g waste limestone
2. 177g trap rock + 123g waste limestone
3. 159g trap rock + 141g waste limestone
4. 126.6g trap rock + 173.4g waste limestone

5. 184.5g basalt #1 + 115.5g waste limestone
6. 300g basalt #3
7. 240g basalt #3 + 60g waste limestone
8. Falconbridge Ni-Cu slag 210.5g + 89.5g quartz
9. 225g pelletized iron slag + 75g quartz
10. 225g air-cooled iron slag + 75g quartz
11. 300g Pacific Enercon Cu slag
12. 224g Noranda reverberatory slag + 76g quartz
13. Basalt #1 243.5g + waste limestone 152.5 + soda ash 4g
14. Basalt #1 241g + waste limestone 151g + soda ash 8g
15. Basalt #1 234g + waste limestone 146g + soda ash 20g
16. Nepheline syenite waste 217g + waste limestone 183g
17. Nepheline syenite waste 180g + waste limestone 220g
18. Nepheline syenite waste 240g + waste limestone 160g
19. Asbestos tailings 200g + sand 200g
20. Asbestos tailings 240g + sand 160g
21. Asbestos tailings 280g + sand 120g
22. Asbestos tailings 210g + Nepheline syenite waste 190g
23. Asbestos tailings 185g + waste glass 215 g
24. Nepheline syenite waste 226g + waste limestone 74g

A minimum of five measurements at different temperatures were carried out on each sample. A least squares analysis of the data based on a temperature activated model of the conductivity was carried out. The resistivity has the form

$$\rho = \rho_o \exp (E_A/kT)$$

where ρ_o is the pre-exponential factor, E_A is the activation energy, k is the Boltzman constant, and T is the temperature in Kelvin.

The sample and data are classified according to the major component as follows:

Group	Samples
I - trap rock	1, 2, 3, 4
II - basalt	5, 6, 7, 13, 14, 15
III - slag	8, 9, 10, 11, 12
IV - nepheline Syenite Waste	16, 17, 18, 24
V - asbestos tailings	19, 20, 21, 22, 23

The data according to these groups follow below:

GROUP I

SAMPLE No. 1 E_A = 1.54 eV $\rho o = 1.36 \times 10^{-4}$ Ω-cm

T(°C)	1472	1427	1379	1332	1278	1228
ρ(Ω-cm)	3.8	4.8	6.5	9.0	13	20

SAMPLE No. 2 E_A = 1.61 eV $\rho o = 6.98 \times 10^{-5}$ Ω-cm

T(°C)	1476	1430	1377	1333	1279	1229
ρ(Ω-cm)	3.1	4.1	6.0	8.2	12	18

SAMPLE No. 3 E_A = 1.62 eV $\rho o = 6.62 \times 10^{-5}$ Ω-cm

T(°C)	1488	1445	1399	1333	1298
ρ(Ω-cm)	2.7	3.7	5.1	8.1	9.7

SAMPLE No. 4 E_A = 2.22 eV $\rho o = 7.82 \times 10^{-7}$ Ω-cm

T(°C)	1519	1467	1419	1363	1317
ρ(Ω-cm)	1.3	2.4	3.4	5.8	8.4

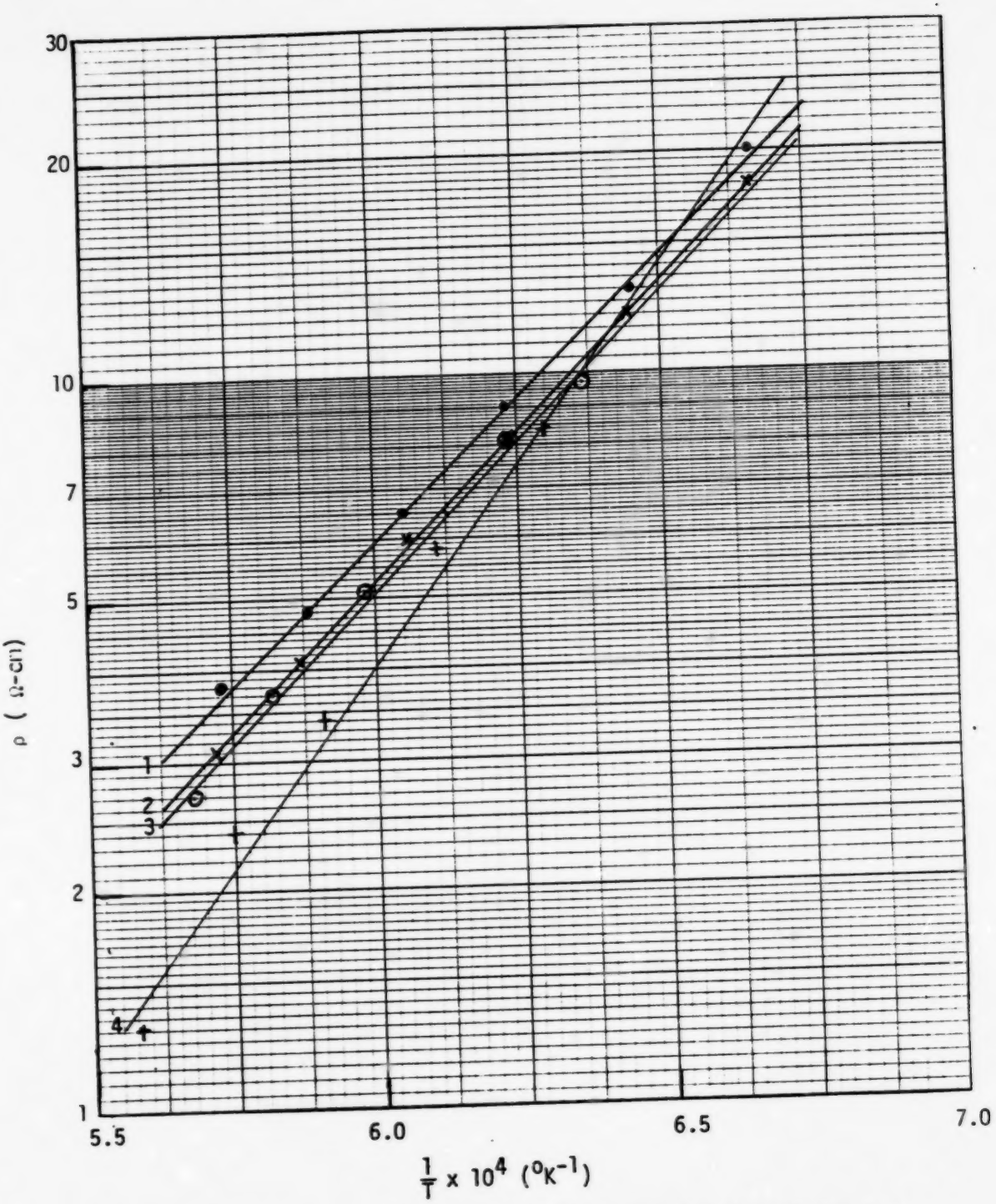


FIGURE 3: Temperature Dependence of the Resistivities of Group I Samples.

GROUP II

SAMPLE No. 5 E_A = 1.59 eV $\rho o = 3.72 \times 10^{-4}$ Ω-cm

T(°C)	1489	1441	1393	1341	1294	1395
ρ(Ω-cm)	14	18	25	33	53	23

SAMPLE No. 6 E_A = 1.89 eV $\rho o = 3.69 \times 10^{-5}$ Ω-cm

T(°C)	1484	1442	1388	1344	1293
ρ(Ω-cm)	9.1	14	20	29	43

SAMPLE No. 7 E_A = 2.00 eV $\rho o = 9.78 \times 10^{-6}$ Ω-cm

T(°C)	1480	1439	1390	1390	1342	1295	1238
ρ(Ω-cm)	5.9	7.7	10	12	17	28	47

SAMPLE No. 13 E_A = 1.37 eV $\rho o = 2.91 \times 10^{-3}$ Ω-cm

T(°C)	1471	1426	1378	1332	1281	1230	1182
ρ(Ω-cm)	26	35	46	61	84	120	160

SAMPLE No. 14 E_A = 1.45 eV $\rho o = 6.42 \times 10^{-4}$ Ω-cm

T(°C)	1468	1420	1342	1282	1202
(-cm)	9.9	14	22	33	58

SAMPLE No. 15 E_A = 1.40 eV $\rho o = 5.42 \times 10^{-4}$ Ω-cm

T(°C)	1476	1433	1362	1293	1206
ρ(Ω-cm)	5.7	7.4	11	16	32

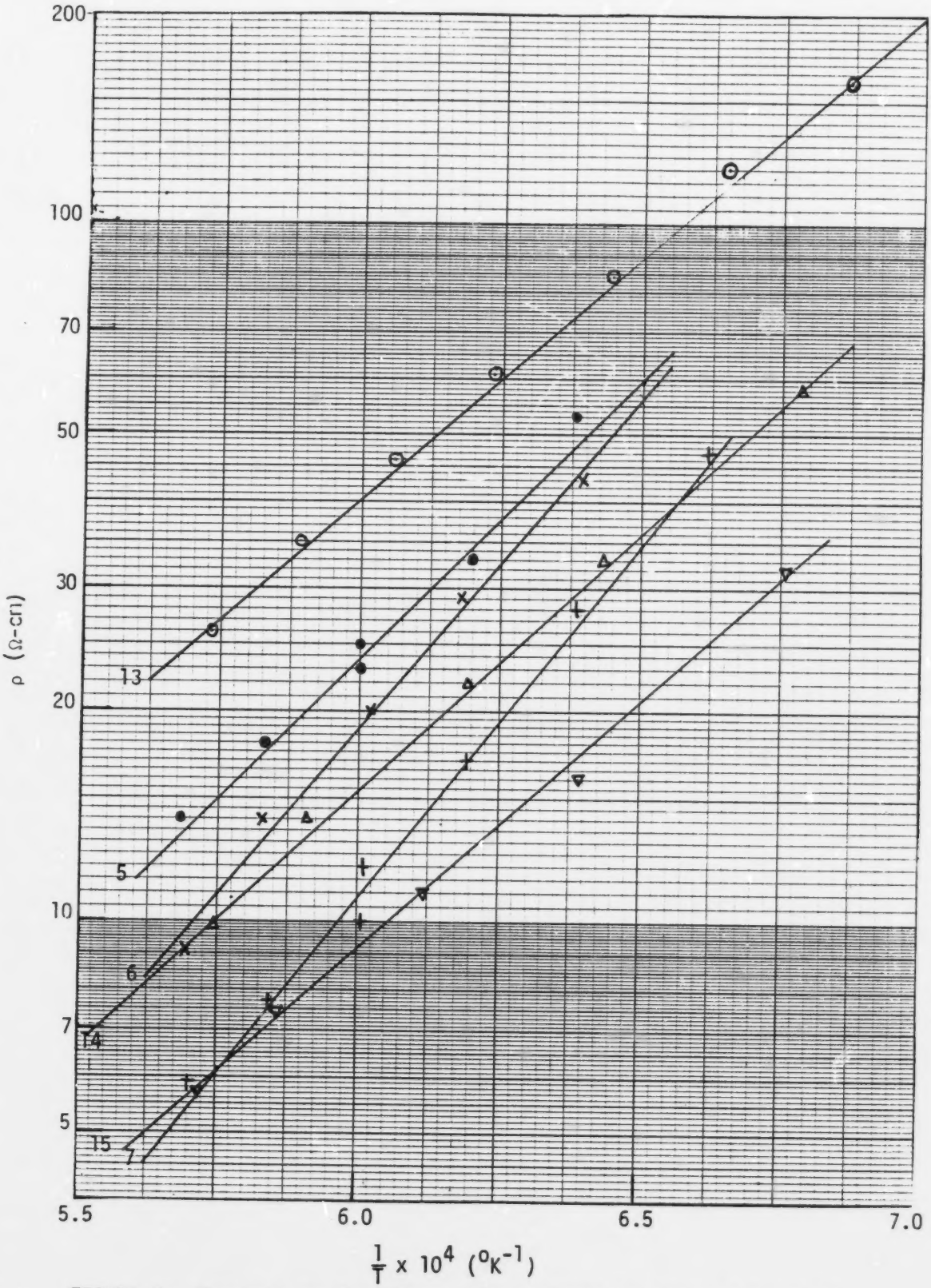


FIGURE 4: Temperature Dependence of the Resistivities of Group II Samples.

GROUP III

SAMPLE No. 8	E_A = 5.45 eV		$\rho o = 1.41 \times 10^{-14}$ Ω-cm		
T(°C)	1547	1533	1521	1509	1496
ρ(Ω-cm)	17	21	26	34	46

SAMPLE No. 9	E_A = 1.86 eV		$\rho o = 3.54 \times 10^{-5}$ Ω-cm			
T (°C)	1480	1438	1394	1338	1287	1485
ρ(Ω-cm)	8.0	11	15	21	36	6.8

SAMPLE No. 10	E_A = 2.04 eV		$\rho o = 9.53 \times 10^{-6}$ Ω-cm			
T(°C)	1489	1442	1387	1338	1289	1235
ρ(Ω-cm)	6.7	9.5	13	20	34	66

SAMPLE No. 11	E_A = 1.69 eV		$\rho o = 5.10 \times 10^{-5}$ Ω-cm					
T(°C)	1476	1433	1382	1334	1281	1229	1180	1134
ρ(Ω-cm)	4.0	5.3	7.4	10	14	25	36	65

SAMPLE No. 12	E_A = 2.30 eV		$\rho o = 5.04 \times 10^{-6}$ Ω-cm		
T(°C)	1551	1540	1531	1521	1507
ρ(Ω-cm)	11	13	14	15	16

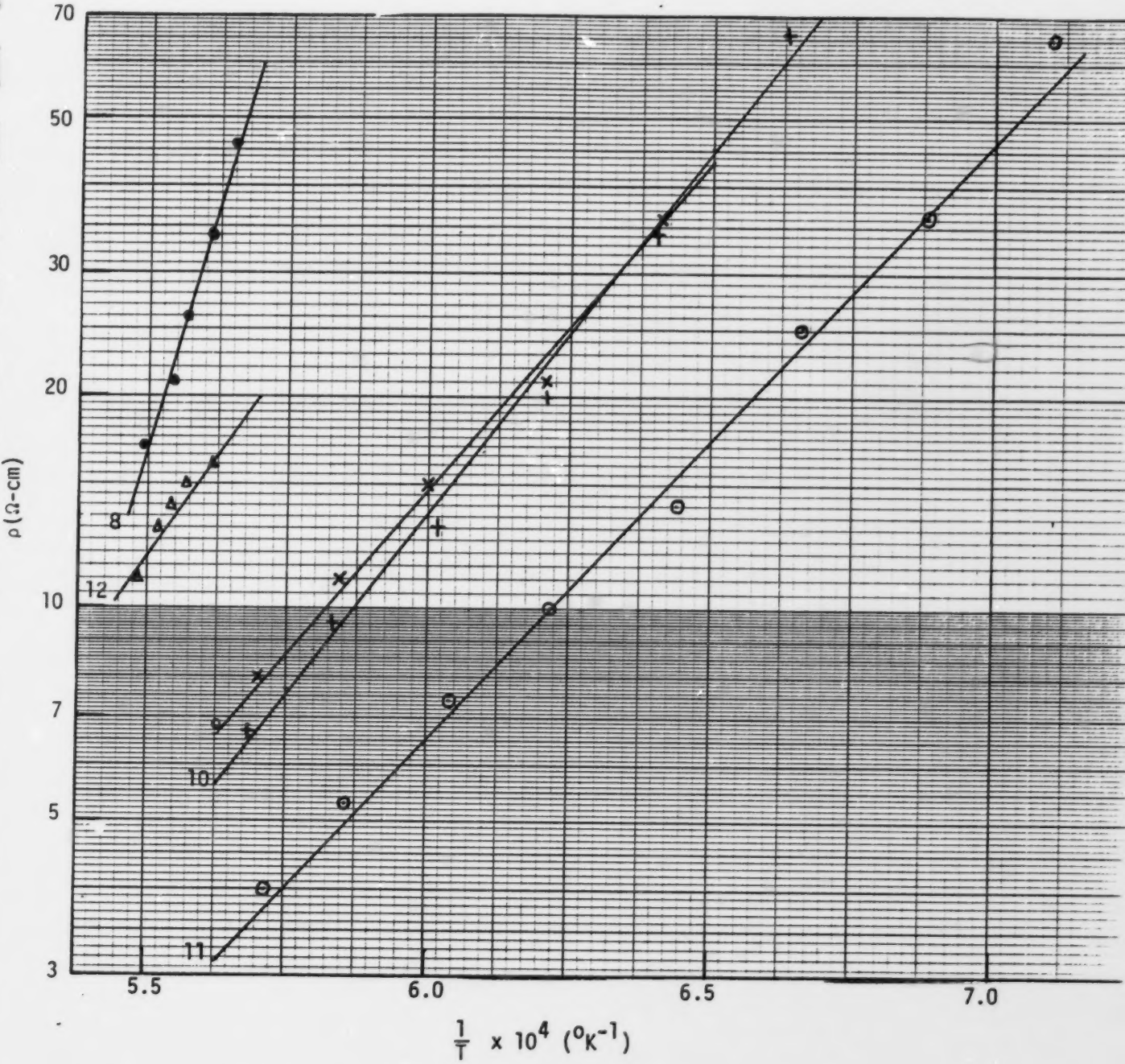


FIGURE 5: Temperature Dependence of the Resistivities of Group III Samples

GROUP IV

SAMPLE No. 16	E_A = 1.57 eV		ρo = 1.65 x 10^{-4} Ω-cm		
T(^oC)	1467	1409	1340	1276	1198
ρ(Ω-cm)	6.1	9.1	12	21	43

SAMPLE No. 17	E_A = 1.50 eV		ρo = 1.67 x 10^{-4} Ω-cm		
T(^oC)	1493	1432	1366	1297	1220
ρ(Ω-cm)	3.3	4.7	6.7	10	21

SAMPLE No. 18	E_A = 1.17 eV		ρo = 2.65 x 10^{-3} Ω-cm		
T(^oC)	1478	1418	1353	1298	1208
ρ(Ω-cm)	6.0	8.5	12	16	25

SAMPLE No. 24	E_A = 1.38 eV		ρo = 9.89 x 10^{-4} Ω-cm		
T(^oC)	1481	1420	1351	1290	1210
ρ(Ω-cm)	9.2	13	19	27	50

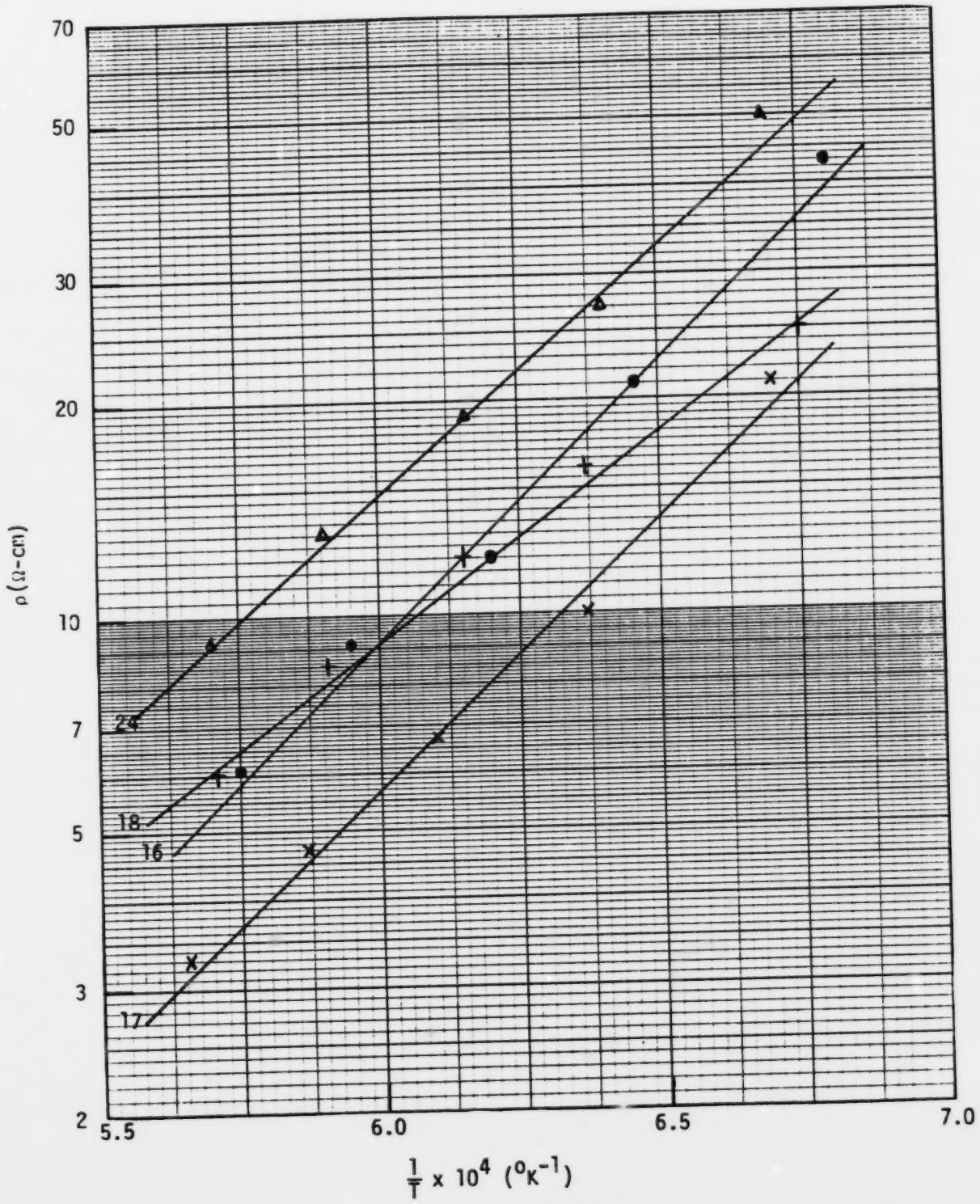


FIGURE 6: Temperature Dependence of the Resistivities of Group IV Samples

GROUP V

SAMPLE No. 19	E_A = 1.98 eV		$\rho o = 3.57 \times 10^{-5}$ Ω-cm		
T(°C)	1533	1503	1480	1447	1423
ρ(Ω-cm)	12	15	18	22	28

SAMPLE No. 20	E_A = 1.63 eV		$\rho o = 1.59 \times 10^{-4}$ Ω-cm		
T(°C)	1514	1485	1450	1409*	1425
ρ(Ω-cm)	6.3	7.6	9.4	23	11

* neglected in analysis since Sample has solidified at this temperature. Recovery on the fifth measurement appears to be complete.

SAMPLE No. 21	E_A = 2.41 eV		$\rho o = 7.01 \times 10^{-7}$ Ω-cm		
T(°C)	1514	1489	1437*	1499*	1459
ρ(Ω-cm)	4.2	5.3	13	6.5	6.9

* neglected in analysis since Sample solidified on the third measuremnt and did not recover until the fifth measurement.

SAMPLE No. 22	E_A = 2.05 eV		$\rho o = 9.17 \times 10^{-6}$ Ω-cm		
T(°C)	1523	1491	1451	1415*	1437*
ρ(Ω-cm)	5.0	6.5	8.7	43	16

* neglected in analysis since the Sample appears to be solidified.

SAMPLE No. 23	E_A = 1.40 eV		$\rho o = 5.79 \times 10^{-4}$ Ω-cm		
T(°C)	1527	1485	1434	1387	1334
ρ(Ω-cm)	4.9	5.9	8.0	11	14

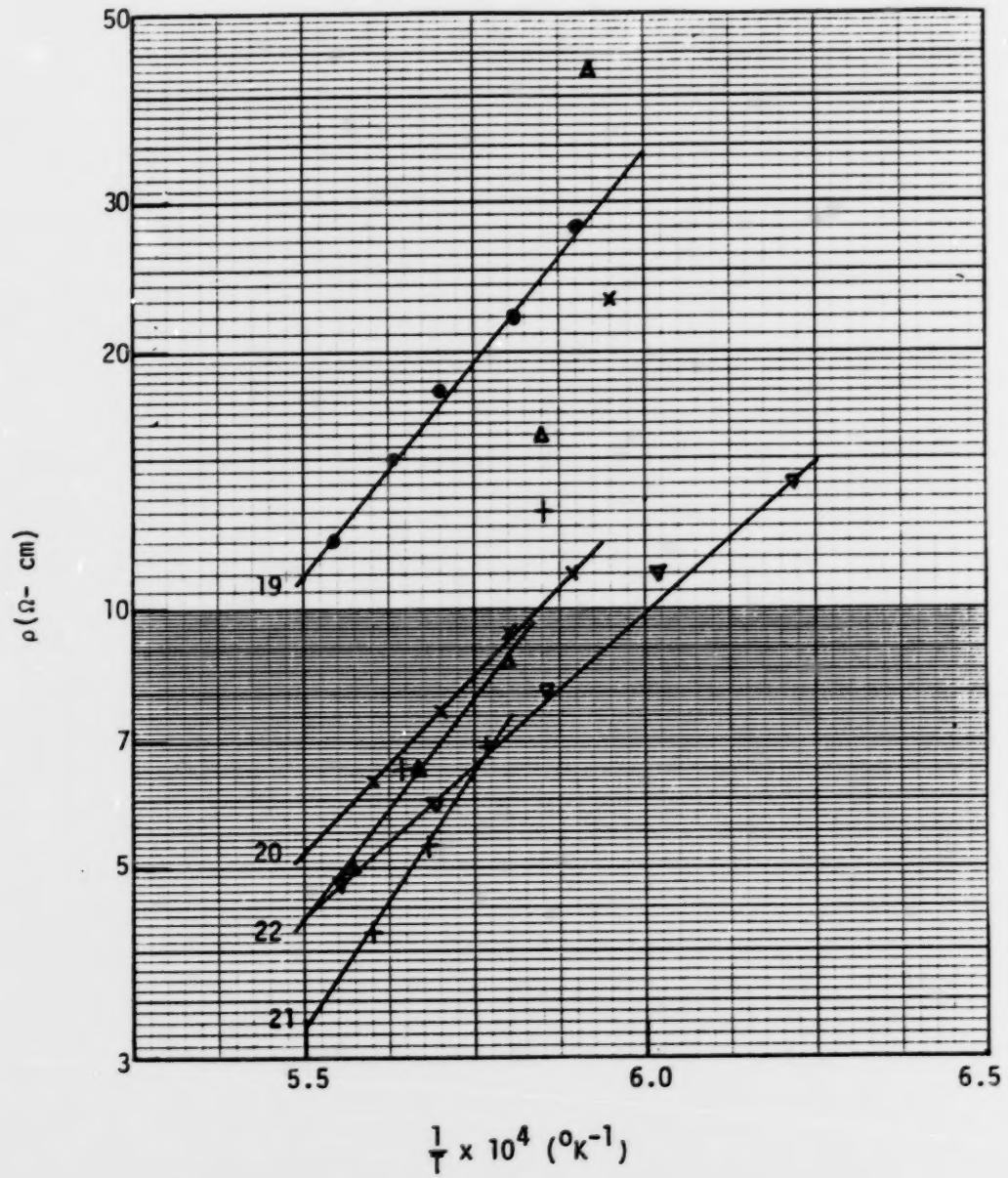
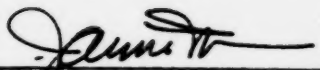


FIGURE 7: Temperature Dependence of the Resistivities of Group V Samples.



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JMR/es

The complex[††] impedance of a linear[†] electrical system is defined by Ohm's law as

$$Z^* = V^*/I^*$$

where the asterisk denotes a complex quantity. The complex admittance is the inverse of the impedance

$$Y^* = (Z^*)^{-1} = I^*/V^*$$

If a harmonic current

$$I^* = I \exp(j\omega t)$$

is passed through the system, the resulting voltage will in general be of a different phase, that is,

$$V^* = V \exp(j\omega t + j\phi)$$

Here, $\omega = 2\pi f$, where f is the frequency; t is the time; and $j = \sqrt{-1}$

The impedance is then given by

$$Z^* = V/I \exp(+j\phi) = Z \exp(+j\phi)$$

or

$$Z^* = Z \cos\phi + j \; Z \sin\phi \; .$$

This is normally written as

$$Z^* = R + j\,X$$

where R is the resistive component and X is the reactive component.

The admittance will be -

$$Y^* = I/V \exp(-j\phi) = Z \exp(-j\phi)$$

$$Y^* = Y \cos\phi - j\,Y \sin\phi$$

$$Y^* = G - jB$$

G is called the conductance while B is called the susceptance of the circuit. The components of the current may be expressed in terms of the components

---

† A linear system is one where the admittance or the impedance are not functions of the applied voltage or current.

††Complex quantities are defined to have a real part, Re(Z*), and an imaginary part, Im(Z*) + jIm(Z*) -- where j is defined to be $\sqrt{-1}$. The exponential function of an imaginary quantity is complex and exp (jωt) can be written in terms of the familiar trigonometric functions as

$$\exp(j\omega t) = \cos\omega t + j \sin\omega t.$$

of the admittance. Under an applied voltage of the form

$$V^* = V \exp(j\omega t)$$

the current will be

$$I^* = V^*Y^* = V^*G - J\, V^*B$$
$$= (I_1 - j\, I_2)$$

The first term I_1 is in phase with the voltage

$$I_1 = VG \exp(j\omega t)$$

called the in-phase component. The second term, however, is of the form

$$-jI_2 = VG \exp(j\omega t - j\pi/2)$$

which is out of phase with the voltage by 90^o. As such, I_2 is called the quadrature component.

The in-phase component is the component that flows through the purely resistive part of the impedance while the quadrature component flows through the reactive part.

The impedance of basic linear elements are

Resistor, R : $Z = R$

Capacitor, C : $Z = -j\frac{1}{\omega C}$

Inductor, L : $Z = j\omega L$

A series arrangement of elements will have an impedance which is the sum of all the impedances.

$$Z_T^* = \sum_k Z_k^*$$

In parallel arrangement, the admittance is the sum of all the admittances,

$$Y_T^* = \sum_k Y_k^*$$

The average power dissipated into heat in a circuit is given by

$$P_{av} = \tfrac{1}{2} VI \cos\phi = V_{rms}\, I_{rms} \cos\phi$$

where V_{rms} and I_{rms} are the root-mean-square values of the voltage and currents and $\cos\phi = \frac{R}{Z}$ is called the power factor. The average power may also be written as

$$P_{av} = I_{rms}^2\, R$$

where R is the resistive component of the circuit impedance.

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